An *Ab Initio* Approach Towards Engineering Fischer-Tropsch Surface Chemistry

Type of Report: Technical Progress Report

Report Period Start Date: 9/11/2001

Reporting Period End Date: 9/11/2002

Principle Author: Matthew Neurock

Original Date Report was issued: June 2003

Modified Report Date was issued: August 2003

DOE Award Number: DE-FG26-01NT41275

Name and Address of Submitting Organization:

Professor Matthew Neurock
Department of Chemical Engineering
102 Engineers' Way
University of Virginia
Charlottesville, VA 22904-4741

DISCLAIMER

I. ABSTRACT

As the US seeks to develop an energy strategy that reduces the reliance on foreign oil, there is a renewed interest in research and development of the Fischer Tropsch synthesis of converting syngas into long chain hydrocarbon products. This report investigates some of the basic elementary steps for Fischer-Tropsch synthesis over ideal Co and Ru metal surfaces by using ab initio density functional theoretical calculations. This includes activation of CO of CO, the hydrogenation of CHx intermediates, and the adsorption and dissociation of water. The activation of CO is studied in detail showing a strong dependence on the surface coverage, defect sites and Co-Ru alloy formation. The barriers for CO activation over the ideal (0001) surfaces are quite high making CO activation at the terrace sites unlikely under operating conditions. The calculations for the overall reaction energies at the step edges indicate that these sites are much more reactive. The hydrogenation of the CHx intermediates occurs in a sequential fashion. CH1 was found to be the most stable intermediate over various surfaces. The barriers to form both CH* as well as CH4 are both found to be highly activated and potentially difficult steps. Water which is a reaction product was found to be weakly adsorbed on Co. Analysis of the microscopic reverse reaction of water activation indicates that this process has a very low activation barrier. Consequently, any water which forms desorbs or is activated to form surface hydroxyl intermediates.

II. TABLE OF CONTENTS

III. INTRODUCTION

Fischer-Tropsch (FT) synthesis is a process that converts CO to more useful hydrocarbons. In the past 70 years since Fischer and Tropsch discovered this process, there have been a large number of studies on the mechanism and the optimal conditions to form the desired products[1-6]. The industrial and governmental investment in the research and development of FT-related processes reflects the change of the economical and political environment. As the US seeks to develop an energy strategy that reduces the reliance on foreign oil, there is a renewed interest in research and development of the FT process. Most of the previous studies have focused on syntheses and characterization of different catalysts. These studies provided essential information for catalyst development and for industrial reactor design. However, a fundamental understanding of the how the atomic scale feature of the catalyst control molecular transformations in FT catalysis is still rather poor.

The overall process of FT synthesis is comprised of a complex network of elementary bond-breaking and bond-formation steps. These steps include CO and H_2 activation as well as hydrogenation and chain growth over supported metals. The balance of the bond breaking and bond formation steps controls the reactivity and selectivity of the process. For example, transition metals to the left in the periodic table will readily activate CO but the products, i.e. surface carbon and oxygen, are too strongly bound to the surface, thus blocking subsequent hydrogenation and carbon coupling reactions. Transition metals to the right, on the other hand, are not active enough to dissociate CO[7,8]. The ideal catalysts for FT synthesis would be those metals that can promote CO activation, along with a balanced degree of surface hydrogenation and hydrocarbon coupling in order to produce longer chain hydrocarbon products. Therefore, analyses of the elementary steps involved in the reaction are important in the search for the best catalysts and the optimal operating conditions. In the present project, we use *ab initio* quantum mechanical methods to analyze the elementary reaction steps over model surfaces involved in the FT chemistry. A schematic of the surface processes is shown in Figure 1. The aim of the project is to gain insight of the reaction mechanisms and to elucidate the structure features that control catalytic performance through a detailed analysis of the elementary steps involved in the process. In our previous efforts we examined CO activation over model Co(0001) and Ru(0001) surfaces and in addition probed the initial CH and CH_2 coupling over Co. In this past year, we extended

our efforts and examined CO adsorption and activation over stepped Co surfaces and Co-Ru surface alloys. In addition, we mapped out the reaction energies and activation barriers for the hydrogenation of all CH_x intermediates over model Co, Ru, and Rh surfaces in order to elucidate the effect of transition metal on hydrogenation performance. Lastly, we began to probe the effect of water on the reactivity and selectivity by examining water adsorption and dissociation over model Co surfaces.

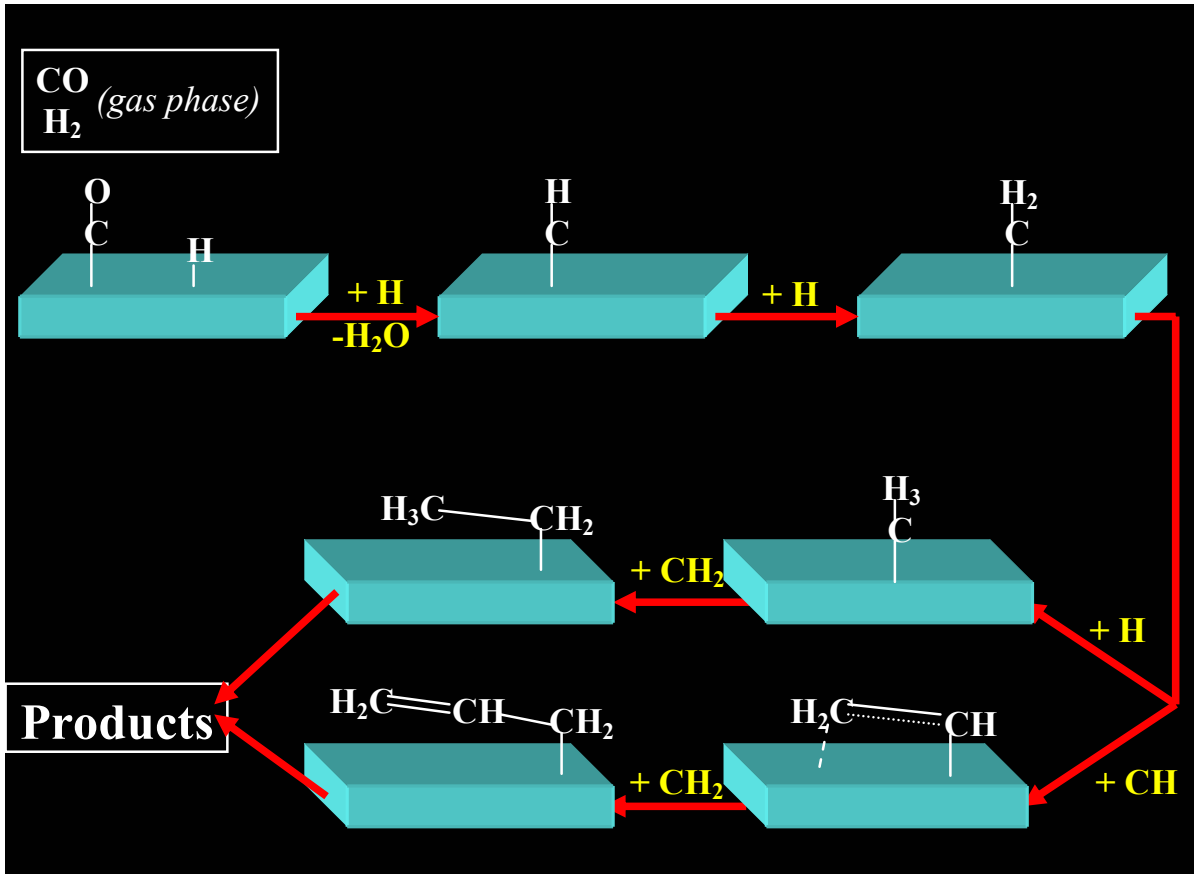

Figure 1. Schematic of elementary surface reaction steps in FT synthesis

IV. EXECUTIVE SUMMARY

Fischer-Tropsch synthesis has had a major resurgence over the past decade as industry, as well as, the government seek to find attractive solutions to energy issues. Most of the previous studies in the literature on Fischer Tropsch have focused on syntheses and characterization of different catalysts and their activity. These efforts have helped to provide guidance in catalyst development and reactor design. There has much less emphasis, however, on the elementary kinetic steps which control catalyst performance. FT synthesis is comprised of a complex network of elementary bond-breaking and bond-formation steps. These steps include CO and H_2 activation, hydrogenation and chain growth over supported metals. We have used *ab initio* quantum mechanical methods here to analyze: 1) the adsorption and activation of CO over stepped Co surfaces and Co-Ru surface alloys, 2) the hydrogenation of all CH_x intermediates over model Co, Ru, and Rh surfaces, and 3) the adsorption and activation of water over model Co surfaces.

Nonlocal gradient corrected density functional theoretical calculations were performed herein to elucidate the mechanisms and quantify the energetics for specific reaction steps. The lattice constants calculated for both Co and Ru were found to be in very good agreement with those reported experimentally.

DFT results for the adsorption of CO indicate that it preferentially sits at the atop sites on both Co as well as Ru with binding energies of 158.6 and 193.0 kJ/mol respectively. The difference between specific sites on Co is very weak (< 9 kJ/mol). The changes are somewhat higher in moving to Ru (~15 kJ/mol). The barriers for the activation of CO were greatly influenced by the surface coverage. The activation barriers for CO over Co and Ru in a 2x2 unit cell (0.25 ML of CO) were calculated to be 230 and 190 kJ/mol respectively. Both of these barriers are high. These steps are therefore not very likely. The barrier for CO activation over Co$\{0001\}$, however, is reduced from 230 kJ/mol (1/4 ML CO coverage) to 140 kJ/mol (at 1/9 ML coverage) by simply decreasing the surface coverage. The presence of steps or defect sites were found to critically affect the overall reaction energies as well as the activation barriers. The overall heat of dissociation over Co$\{10\bar{1}2\}$, Co$\{11\bar{2}0\}$, and the $\{11\bar{2}4\}$ were found to be –71 kJ/mol, 54 kJ/mol, 38.8 kJ/mol. The dissociation of CO on the $\{11\bar{2}0\}$ and $\{11\bar{2}4\}$ surfaces were still endothermic but much more favorable than that for CO on Co$\{0001\}$. The overall reaction energy over the $\{10\bar{1}2\}$ surface was actually found to be exothermic. Lastly we found that alloying Co with Ru increases the binding energy of CO and thus helps to enhance CO activation. CO activation over Co$\{0001\}$ was found to be endothermic (56.8 kJ/mol) whereas its activation over the alloy was found to be exothermic at -10.8 kJ/mol.

The surface carbon that forms can subsequently be hydrogenated to different CH_x intermediates. A balanced degree of hydrogenation is needed in order to produce longer chain hydrocarbons. Complete hydrogenation will lead to the formation of methane whereas incomplete hydrogenation will lead to coke both of which are undesirable. We therefore systematically examined the sequential hydrogenation of surface carbon all the way to methane over both Co$\{0001\}$ and Rh(111) substrates for comparison. The CH intermediate was found to be the most stable surface intermediate over both Co and Rh. The activation barriers (and overall reaction energies) were found to be +74 (-35), +55 (+34), +40 (-30) and +86 (-11) kJ/mol for the

reactions of C_a+H_a, CH_a+H_a, $CH_{2a}+H_a$, $CH_{3a}+H_a$ respectively. The addition of the first hydrogen to form CH and the last hydrogen to form methane which are the most stable intermediates were found to be the most difficult steps. The transition states for each of these hydrogenation steps are quite early along the entrance of the reaction channel. This is reflected by the rather long separation between CH_a and the H_a. The major contribution to the activation energy is therefore expected to come from the activation of the reactant states. The activation barrier calculated here for the Ca hydrogenation, a potentially limiting step, is found to be quite close to that which we had found previously for $CH+CH_2$ coupling, an important chain growth. This might suggest that there is an optimal balance between hydrogenation and coupling steps. This is important in the synthesis of longer chain hydrocarbons which require that indeed both steps be kinetically in balance.

Water which is formed as a main product in Fischer-Tropsch can influence the rates and as well as the product distributions that form. In some studies water has been found to enhance the rates whereas in others it impedes the rate. Our initial studies have used ab initio calculations to probe the stability of water on the model Co{0001} surface. The results show that water adsorbs weakly to Co{0001) at -36.3 kJ/mol. The overall reaction energy for the activation of water was found to be -47.9 kJ/mol over Co{0001}. The barrier for this step was found to be very low. The results suggest that water which forms as the result of Fischer Tropsch will either readily desorb or reactivate to form surface OH and H intermediates. It has a rather short life time on the surface as molecularly adsorbed water.

V. COMPUTATIONAL METHODS

The work described herein was carried out using plane-wave density functional periodic slab calculations as implemented in the VASP code developed by Kresse and coworkers[9-14]. The electron-ion interactions were described by ultrasoft pseudopotentials[15] with a plane-wave cut off energy of 320 eV. The Perdew-Wang form (PW91) of general gradient corrections was used to calculate the exchange and correlation energies[16]. Supercells of varying cell sizes and number of metal layers were used in order to model different surface structures. The Monkhorst-Pack[17] mesh was used to sample the surface Brillouin zone. Throughout our calculations, we used a one-sided slab approach, i.e. placing adsorbates on one side of the slab. The atoms of the adsorbates and those in the topmost layers of the metal slab were allowed to optimize according to the forces calculated quantum mechanically.

Activation energies are critical to establishing kinetics. By definition, the transition state is a stationary point along the reaction path at which the tangential force is zero and one of the eigen frequencies is imaginary. As the search for transition states on a complex hyperpotential energy surface is a difficult task, there have been continued efforts to develop methods that can determine the transition state more robustly. In the present calculation, we used the nudged elastic band technique developed by Jonsson and coworkers[18] as implemented in VASP.

VI. RESULTS AND DISCUSSION

A) Results for the Bulk Co and Ru Metal and the Adsorption of CO on These Surfaces.

To construct model surfaces, we first calculated bulk metal properties. The calculated lattice constants are listed in table 1. Spin-polarization is included in the calculations involving Co as it is ferromagnetic. The inclusion of spin-polarization significantly increased the size of the calculation, hence demanded more computer power.

Table 1. Calculated Co and Ru bulk lattice parameters.

	Co		Ru	
	Theory	Exptl.	Theory	Exptl.
a (Å)	2.527	2.507	2.730	2.71
c (Å)	4.089	4.069	4.302	4.28

We further examined CO adsorption on the close-packed Co and Ru surfaces where detailed experimental structures are available. These calculations serve as a test bed for the model chosen for a specific reaction and for the quality of the calculations with the parameters used. The adsorption of CO at different sites on the {0001} surface of both Co and Ru was calculated. The calculations were performed with (√3×√3)R30° and (2x2) surface unit cells. Binding energies at various high symmetry sites in a (√3×√3)R30° were determined, as shown in table 2. On both surfaces, an atop site is the favorable adsorption site, with the potential energy surface of CO on Ru being slightly more corrugated than on Co. On both surfaces, the calculated structures and energies are in good agreement with those from experiments[19,20]. The results for CO on Co is shown in Figure 2.

Table 2. Binding energies of CO on Co and Ru(0001), in kJ/mol

	Atop	Bridge	fcc hollow	hcp hollow
Co	158.6	158.7	156.3	150.7
Ru	193.0	186.2	181.4	178.5

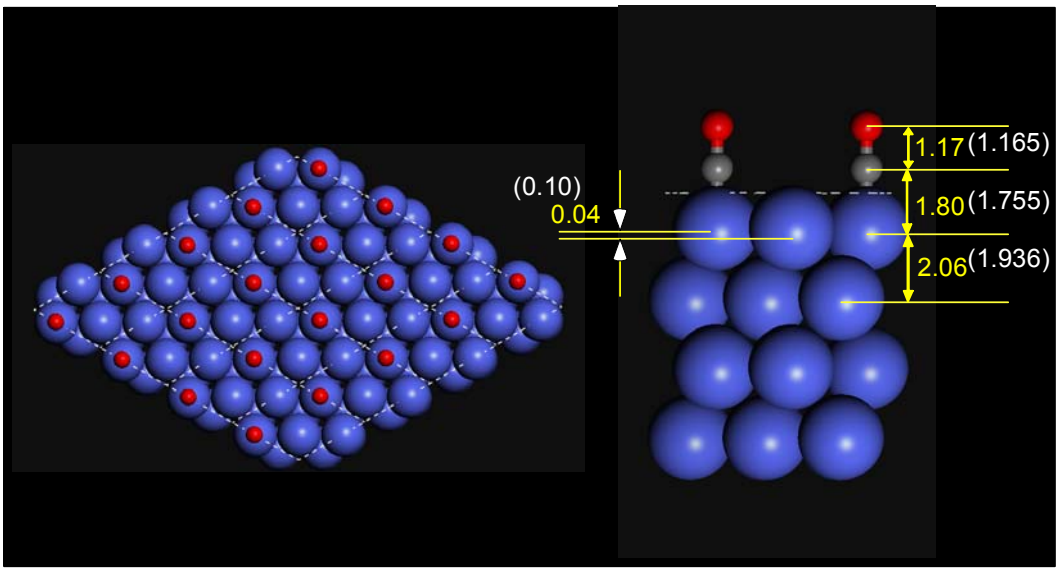

Figure 2. Comparison of structures for chemisorbed CO on Co{0001} from the current calculation, shown in parentheses, and those from a LEED experiment[19].

B. Effect of Coverage on CO Dissociation

We showed previously that the adsorption of CO on both surfaces is quite strong and that dissociation is fairly endothermic, with heats of reactions of 150 and 120 kJ/mol on Co and Ru, respectively. On a close-packed surface, two possible low energy pathways were identified by examining the symmetry of the surface, as shown in Figure 3[21]. Along path I, CO at the transition state sits on two adjacent bridge sites of the close-packed atoms. The C-O bond is further stretched after passing the transition state and O falls into the next hollow site. Along path II, CO dissociates across the atop site of a surface metal atom. The final state corresponds to the C and O adatoms occupying the inequivalent hollow sites on the opposite sides of the Co atom. We showed that the two pathways calculated with a (2x2) surface unit cell have similar activation barriers and the barriers for CO dissociation are high at about 230 and 190 kJ/mol over Co and Ru, respectively.

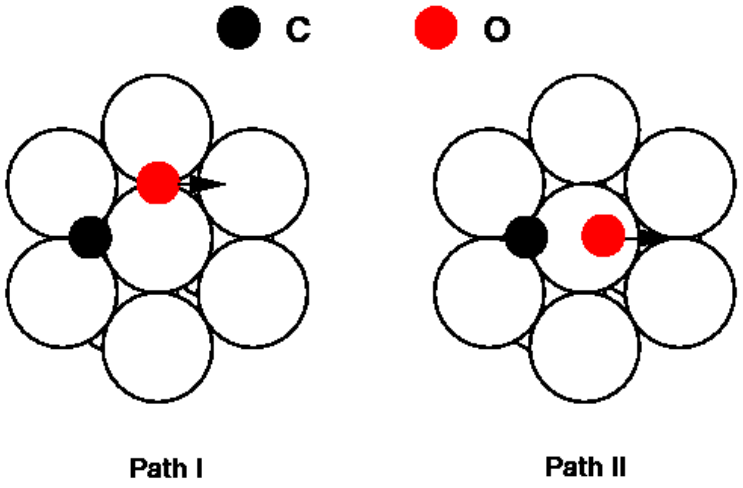

Figure 3. Two possible dissociation pathways for C–O bond activation on a close-packed surface.

In our more recent studies we find that surface coverage has a strong effect on the activation barriers for CO dissociation. When chemisorbed CO forms a $(\sqrt{3}\times\sqrt{3})R30°$ overlayer, corresponding to a coverage of 1/3 of a monolayer, CO dissociation will proceed because of the high coverage. When the reaction occurs on a (2×2) surface unit cell, corresponding to a coverage of ¼ of a monolayer, we noticed that there was metal-sharing at both the transition state and the final state. This is particularly apparent for path I, as the distance between the neighboring O and C adatoms is only 2.5 Å, i.e. one lattice spacing. This small separation

between the two strongly adsorbed adatoms is likely to induce strong repulsive interactions between them. As a matter of fact, the C and O coadsorbed in a (2×2) surface unit cell is approximately 65 kJ/mol higher in energy than that of the C and O adatoms calculated separately in a (2×2) unit cell. In the later case the distance between the adatoms is more than 5 Å. The strong repulsive interaction between C and O in the final state is likely to push up the energy of the transition state. Consequently, this will lead to the increase of the reaction barrier.

To examine the effect of these repulsive interactions on the reaction barrier, we performed a calculation at a lower surface coverage. This system is modeled by using a (3×3) surface unit cell, corresponding to a coverage of 1/9 of a monolayer. At this coverage, the

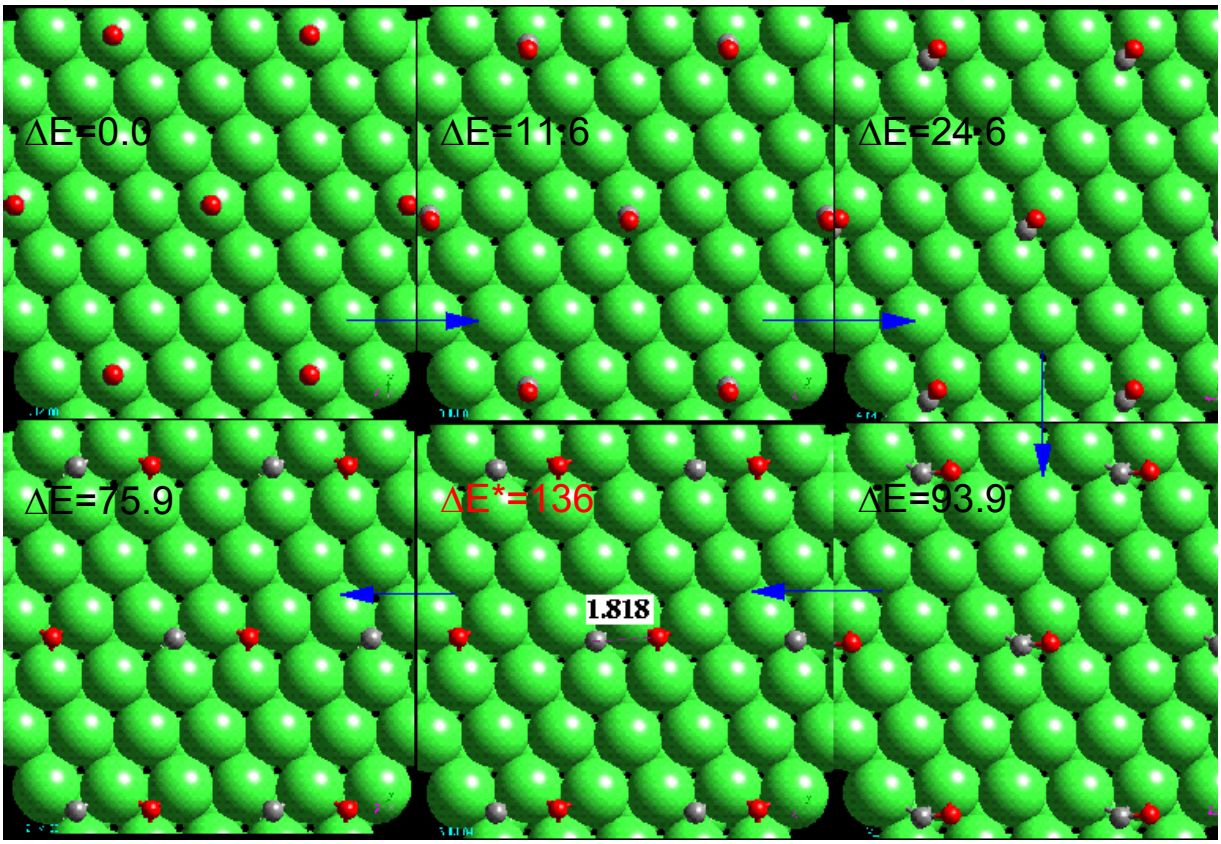

Figure 4. Images of CO dissociation over Co{0001} in a (3×3) surface unit cell along the pathway that starts from CO chemisorbed on an atop site and forms C and O adatoms in hcp hollow sites. The pathway follows the blue arrow from top left to bottom left. The energies on each image are calculated with respect to the initial state. The activation energy of this pathway is shown in red.

overall reaction becomes less endothermic and the energy difference between the initial and final state decreases from ~130 kJ/mol to ~ 76 kJ/mol. The calculated activation barrier for CO dissociation is also decreased from ~230 kJ/mol to ~ 140 kJ/mol, significantly lower than that from the (2×2) surface unit cell calculations. Figure 4 shows a sequence of images along the reaction coordinate from initial state to the final state together with the energies with respect to the initial state. At the transition state, the C—O bond is stretched to 1.82 Å.

C. Effect of steps on CO dissociation over Co.

The reaction barrier for CO dissociation on the flat Co{0001} surface is obviously very high, from both our own results and from the literature, even at coverage as low as 1/9 ML. The very high barrier is consistent with the experimental observation that CO dissociation does not occur over Co{0001}[22]. The presence of defect sites such as steps and kinks have been shown both experimentally and theoretically to strengthen the chemisorption bond between the adsorbates and the surface[23,24]. These high binding energy sites are believed to have superior catalytic reactivity for bond-breaking processes. Therefore, defect sites may play important roles in CO dissociation[25]. In the present study, the following surfaces, $\{10\bar{1}2\}$, $\{11\bar{2}0\}$ and $\{11\bar{2}4\}$, have been constructed in order to examine the effect of defect sites on CO dissociation. Figure 5

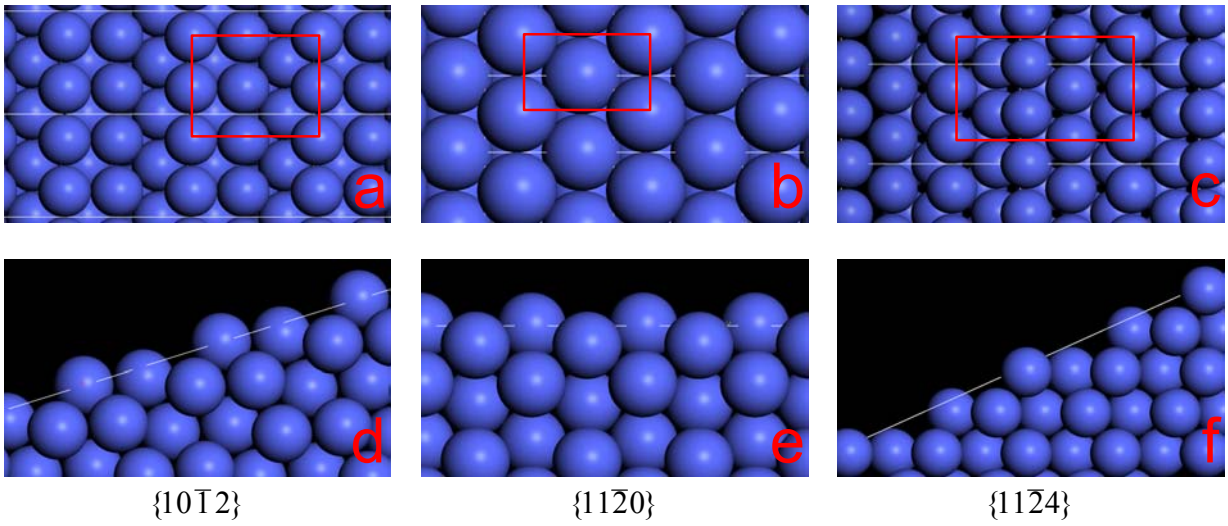

Figure 5. Top (a, b, c) and side (d, e, f) views of $\{10\bar{1}2\}$, $\{11\bar{2}0\}$ and $\{11\bar{2}4\}$ surfaces. The unit cell for each surface used in our calculations is depicted in the top views. The side view shows the corrugation of the surface and the surface steps in each case.

shows the structures of the three surfaces. The $\{11\bar{2}0\}$ surface is more open and corrugated than the close-packed $\{0001\}$ surface although there is no step on the surface. Both $\{10\bar{1}2\}$ and $\{11\bar{2}4\}$ contain steps, as shown in figure 5, with the latter having double steps in one unit cell. We expect that the stepped surfaces will be more active for CO dissociation.

We first examined CO, C and O adsorption over these surfaces. Figure 6 and 7 show carbon and oxygen adatoms occupying different adsorption sites on the $\{10\bar{1}2\}$ surface, respectively. For a carbon adatom, the most stable site is the pseudo four-fold site close to the step edge, as shown in figure 6B. Metastable sites such as those shown in figure 6A, C and D are also isolated. In figure 6A, carbon is adsorbed in between the bridging Co atoms on the step edge. On the other hand, a carbon atom occupies a three-fold-like site consisting of step and lower terrace Co atoms in figure 6C. The binding energy in this site is lower than the most stable carbon adsorption configuration by 67.2 kJ/mol. In figure 6D, a carbon adatom is adsorbed in a four-fold like site consisting of Co atoms from the both upper and lower terraces. In fact, the starting geometry for this configuration was the carbon adatom in the pseudo three-fold site right next to the fourfold site on the terrace. The relaxation process moved the carbon adatom to the final site and pulled the rows of Co atoms from the upper and lower terraces to form the final adsorption structure. The strong binding of carbon atom with the surface counterinteracts with the reconstruction of the surface Co atoms, which results in a less strongly bonded state in this site as shown figure 6D.

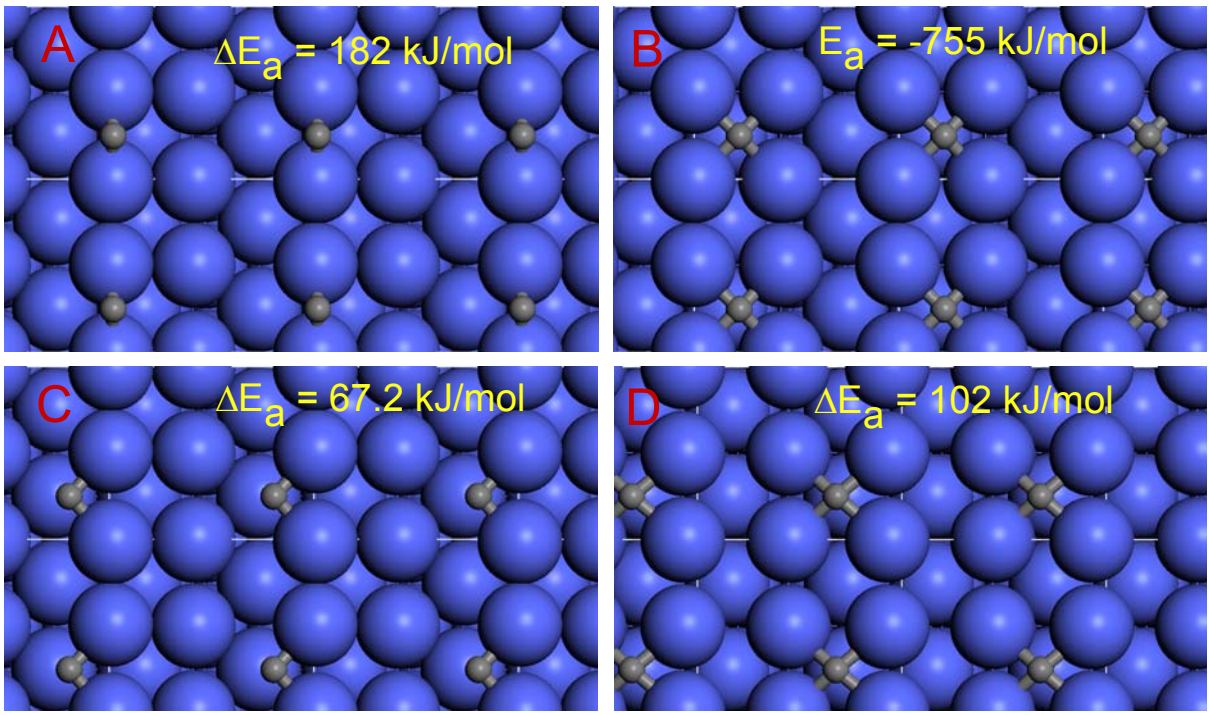

Figure 6. Top view of C adsorption on a Co $\{10\bar{1}2\}$ surface. The most stable site is a pseudo four-fold site, with a binding energy of 755 kJ/mol. Other configurations, A, C and D are less strongly bonded than B, with the difference shown in the corresponding image.

Similarly, oxygen adsorption shows some variations across the stepped surface, although the variation is much less pronounced than that for carbon. For an oxygen adatom, starting from the bridge site on the step edge leads to an almost identical final configuration as that from the fourfold site, as shown in figure 7A and B. In contrast with the case of carbon adsorption, we found that both three-fold sites on the terrace and on the step are metastable for oxygen adatoms. The binding of oxygen with the surface is not strong enough to pull the Co atoms from upper and lower terraces to form a fourfold like site, as in the case of C.

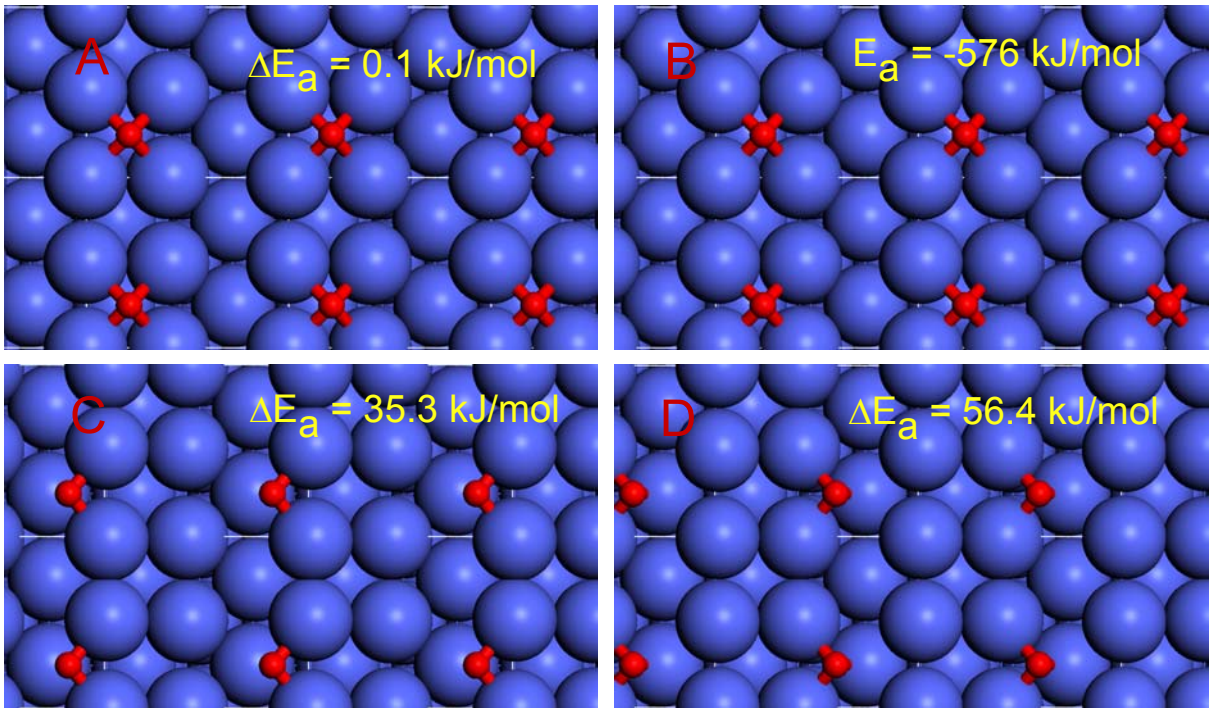

Figure 7. Top view of O adsorption on a Co $\{10\bar{1}2\}$ surface. The most stable site is a pseudo four-fold site, with a binding energy of 576 kJ/mol. Other configurations, A, C and D have lower binding energy than B, with the difference shown in the corresponding image.

As CO generally prefers to occupy an atop site, there should not be significant changes in CO adsorption energies on different surfaces. The binding energy of CO on the atop site close to the step edge of Co $\{10\bar{1}2\}$ is 160 kJ/mol. We also computed CO as well as C and O adatoms on $\{11\bar{2}0\}$ and $\{11\bar{2}4\}$. The results are collected in table 3.

According to these results, the dissociation of CO is still endothermic on both $\{11\bar{2}0\}$ and $\{11\bar{2}4\}$, and is not significantly more favorable than on the $\{0001\}$ surface. In contrast, the reaction over the $\{10\bar{1}2\}$ surface becomes exothermic. Based on knowledge from the literature and our own experience, the dissociation of CO has a late transition state, i.e., the transition state resembles the product

Table 3 Comparison of CO, C and O adsorption energies on different Co surfaces, in kJ/mol

	$\{10\bar{1}2\}$	$\{11\bar{2}0\}$	$\{11\bar{2}4\}$	$\{0001\}$
CO	160	163	157	159
C	755	684	719	659
O	576	524	499	543
ΔH_{rxn}	**-71.2**	**54.8**	**38.8**	**56.8**

state[21]. We would therefore expect that the major factors contributing to the change of the CO dissociation barrier with respect to the close-packed surface would be the extra stabilization of the product state, i.e., O and C adatoms, provided by the steps. We are in the process of screening the possible reaction pathways and searching for transition states for different reaction pathways. The results of these calculations will be reported in the future.

D. Effect of Alloying Co with Ru on CO Adsorption and Dissociation

Ruthenium is often used as a promoter in Co-based catalysts and has been proven to effectively improve the activity of the catalysts[26,27]. However, Ru is a rare element and only mined with other precious metals in small quantities. Therefore, understanding the mechanism with which Ru promotes a Co-based catalyst is both economically and scientifically important. In the present project, we studied CO adsorption on uniform Ru-Co surface alloys supported on both Co and Ru substrates to examine the effect of the presence of a second metal, in particular when they form a surface alloy, on the strength of the CO-surface bond and on the reaction pathways. The adsorption calculation has been performed with a $(\sqrt{3}\times\sqrt{3})R30°$ unit cell. The calculated CO adsorption energies on various sites at different surface compositions are listed in table 4. We note that the binding energy of CO on Co sites over the surface alloy formed on Ru substrate is greatly increased with respect to that on the pure Co surface. On the other hand, the CO chemisorption bond is slightly weakened on the Co site over the surface alloys supported on a Co substrate. This can be explained as Co has a smaller lattice spacing than Ru and supporting a surface alloy of Co-Ru induces strain within the layer of the surface alloy. The small distance between Co and Ru may cause a charge redistribution between Co and Ru. The charge transfer from Ru to Co will impede the ability of Co to accept charge from a CO molecule, and consequently weakens the chemisorption bond of CO formed on the Co site[28]. We also started to examine CO dissociation

Table 3. CO adsorption energies on Co-Ru surface alloys, in kJ/mol

Composition		0.33	0.66	1.00
Co on Ru	Co site	182	186	181 (top)
	Ru site	198	205	179 (hcp)
Ru on Co	Co site	153	143	145 (hcp)
	Ru site	190	173	205 (top)

over the surface alloys. Our preliminary results showed that CO dissociation can be exothermic over the surface alloys. For example, CO dissociation over the Co site on Co-Ru surface alloy supported on Ru substrate at a Co composition of 0.33 is exothermic with heats of reaction of -10.8 kJ/mol. We will continue to study CO dissociation over surface alloys with different compositions and substrates.

E. Hydrogenation of Surface CH_x Species

Hydrogenation is an essential step in order to synthesize high hydrocarbons from CO. It has been studied extensively as the reversal process of C-H bond cleavage in methane activation to produce syngas. Naturally, hydrogenation of surface carbonaceous species is desirable in FT synthesis. However, a balanced degree of hydrogenation needs to be achieved in order to produce long chain hydrocarbons. Hydrogenation of the surface carbonaceous species all the way to methane is not desirable and this is the very reason that Ni does not make a good catalyst for FT processes. Instead, Ni-based catalysts are widely used for the water-gas shift reaction.

We studied systematically the hydrogenation steps from surface carbon all the way to methane over the close packed {0001} surface of Co and Ru as well as Rh{111}. The adsorption structures and energies of individual species as well as coadsorbed species have been calculated. Dissociation of methane in gas phase is a highly endothermic process and the energy cost to completely break CH_4 into the gas phase C and H atoms is 1764 kJ/mol. This process becomes much less endothermic on the surface as the heat of the reaction on Co{0001} is only 20 kJ/mol. In table 5, we list the reaction energies to break CH_4 into a series of surface CH_x species and H adatoms. The results for Ru are taken from the literature, which were produced by our collaborators in Holland[29,30]. Clearly, CH is the most stable C_1 hydrocarbon on Co and Ru. The hydrogenation process from CH_a to methane is thermodynamically unfavorable over these two metals. On the other hand, Rh favors the formations of surface CH_2 species. Provided with the

Table 4. Dissociation energies of methane to different products over Co{0001}, Ru{0001} and Rh{111}, in kJ/mol.

	Co	Ru*	Rh
$CH_{4,g} \rightarrow CH_{3,a} + H_a$	1	-6	1
$CH_{4,g} \rightarrow CH_{2,a} + 2H_a$	21	-11	-35
$CH_{4,g} \rightarrow CH_a + 3H_a$	-13	-56	9
$CH_{4,g} \rightarrow C_a + 4H_a$	20	-21	16

right balance of energetics for the coupling reaction and the surface coverage, these CH_x species should actively participate in chain-growth reactions.

We further calculated activation barriers for each individual hydrogenation step on the three surfaces. In figure 8, we showed a top view of initial, transition and final states of these

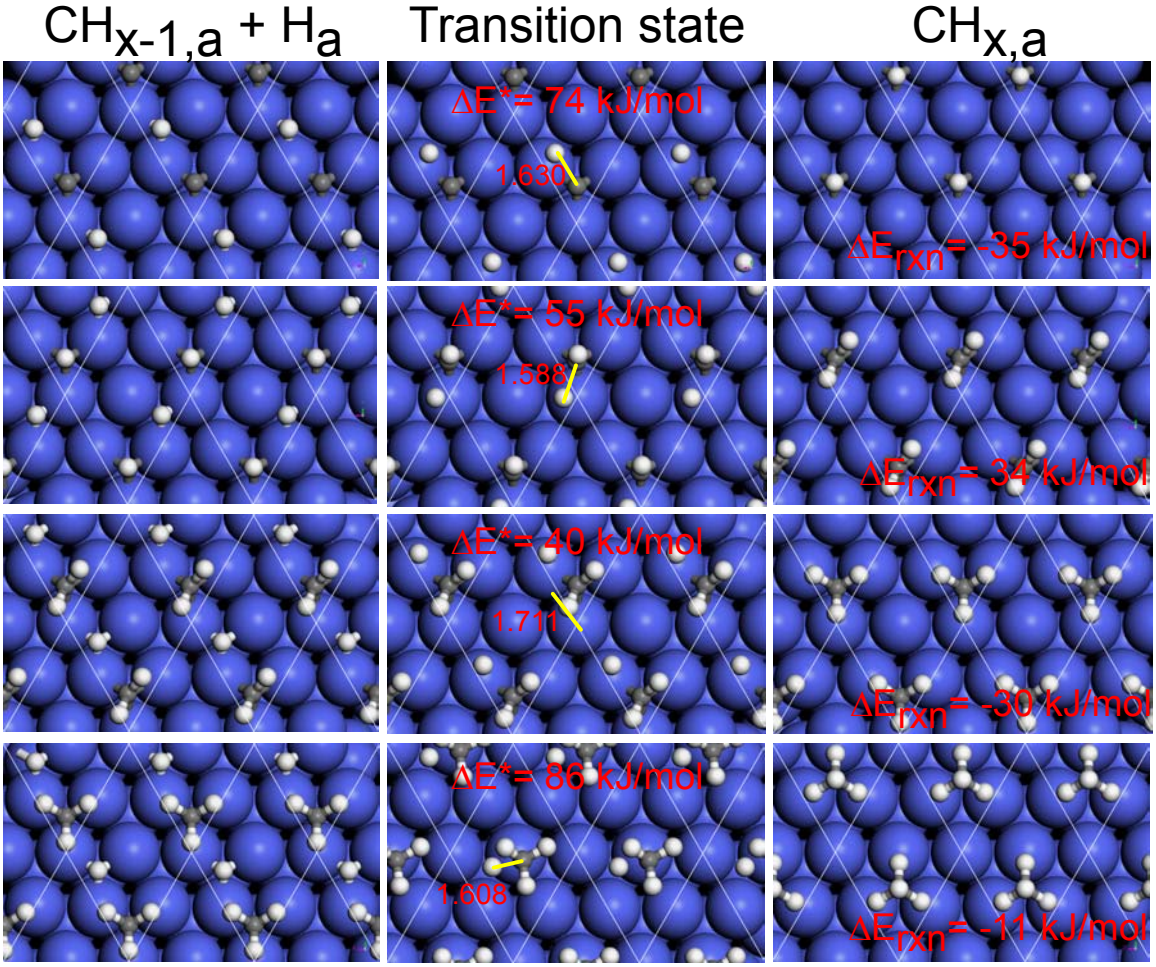

Figure 8. Energetics of CH_{x-1} hydrogenation process over Co{0001}. From top to bottom, $C_a + H_a \rightarrow CH_a$; $CH_a + H_a \rightarrow CH_{2,a}$; $CH_{2,a} + H_a \rightarrow CH_{3,a}$; $CH_{3,a} \rightarrow CH_{4,a}$. The activation barrier and reaction energy of each step are shown in the corresponding subset. The barrier and reaction energy are calculated with respect to the initial state for each step.

steps over Co{0001}. The lateral interaction energy between $CH_{x-1,a}$ and H_a in the initial reactant states was included in the calculation of the reaction energy and activation barrier of each step. The results indicate that the hydrogenation of surface C has a rather high barrier, ~74 kJ/mol,

although this step is exothermic. This is because the activation barrier for the hydrogenation step lies in the entrance channel of the transition state. The "early" transition state of the hydrogenation step is reflected by the rather long separation between the H adatom and the C atom of the CH_{x-1} species, >1.6 Å. Therefore, the major contribution to the activation energy is expected to come from the activation of the reactant state, i.e. the strongly adsorbed C and H adatoms. The stability of the product state contributes little to the activation energy of this step. The last step of the hydrogenation, i.e. $CH_{3,a} + H_a \rightarrow CH_4$, is also highly activated. This can be attributed to the steric constraint of the adsorbed CH_3 which makes it difficult for H to attack.

F. Water Adsorption and Dissociation over Co{0001}

Water formed during conversion of H_2/CO to hydrocarbons has been found to increase reaction rates, as well as the molecular weight and olefin content in the products. However, higher water concentration causes irreversible oxidation of Co crystallites and loss of catalytic activity[4,31]. As a first step towards the understand of the effect of water on the major reaction steps leading to hydrocarbon formation, we studied the adsorption and stability of water on Co{0001}. The aim of these calculations is to determine in what form water exists on the Co-based FT catalyst.

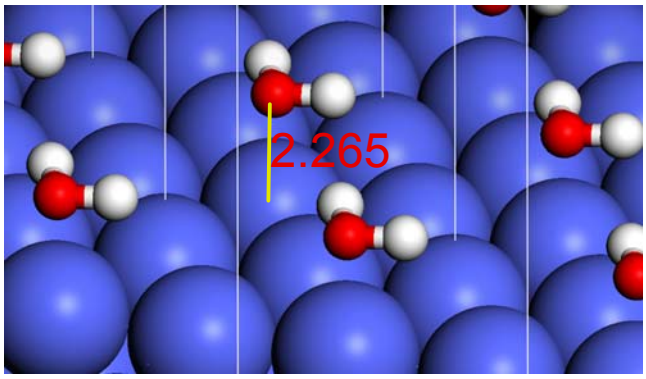

Figure 9. The most stable adsorption configuration of water on Co{0001}.

Figure 9 shows the most stable adsorption configuration of water on Co{0001}. This atop site adsorbed water has its oxygen atom almost directly on top of the surface Co atom. The distance between the oxygen atom and the Co atom is 2.265 Å. The long separation between water and the surface leads to a weakly bound water. The heat of adsorption of water at this site is 36.3 kJ/mol. This value is in general agreement with water adsorption on most of the metal surfaces: water tends to bind to the surface weakly. Therefore, water has a relatively flat

potential energy surface on Co{0001} and there are many sites and adsorption configurations that have adsorption energies in the range of 20 to 36.3 kJ/mol.

We further examined water dissociation over the Co{0001} surface. The results show that water dissociation over the surface is thermodynamically favorable, with a reaction energy of -49.2 kJ/mol from adsorbed H_2O. The dissociation of adsorbed OH species to H and O adatoms is also exothermic, with a reaction energy of -47.9 kJ/mol. A transition state search for the first step of water dissociation, i.e. $H_2O_a \rightarrow OH_a + H_a$, showed that this reaction is almost barrierless on Co{0001}. Consequently, water formed during FT synthesis will most likely exist as coadsorbed hydroxyl groups and hydrogen adatoms, depending on the partial pressure of water and hydrogen. The high coverage of surface hydrogen and other atomic species may prevent H_2O from breaking up. We plan to construct model systems to study the effect of water on other elementary steps, in particular those steps involving surface hydrogen.

VII. CONCLUSION AND FUTURE EFFORTS

Using first principles density functional theory, we analyzed some of the most important elementary steps in Fischer-Tropsch synthesis. We showed that activation of CO over close-packed surfaces, in particular, over Co{0001}, is a highly activated process and is sensitive to the surface coverage. More open surfaces with specific arrangements of step atoms may provide active sites for CO activation.

CH is the most stable C_1 hydrocarbon species on both Co and Ru surfaces. Hydrogenation of surface carbon to CH must overcome significant barriers.

Dissociative adsorption of water on Co{0001} is a thermodynamically favorable process. Molecularly adsorbed water is weakly bound on the surface and is metastable. The adsorbed water molecule on the surface has a flat potential energy surface.

In the next year of this program, we will investigate the effects of surface coverage on the hydrogenation of the CHx surface intermediates. In addition we will complete the studies on CHx coupling reactions. This will provide us with an initial database for which we can begin to simulate the working surface kinetics. Building upon the understanding of the FT chemistry from ab initio quantum mechanical studies of the elementary steps and mechanism of the process, we will construct a kinetic Monte Carlo model of the process by including all the possible chemical

steps. A schematic of the possible events is shown in Figure 10. The binding energies of the surface species and the activation barriers calculated from *ab initio* calculations will be used in the Monte Carlo simulation to follow the time evolution of the process. Parameters for a micro kinetic model can be obtained from the simulation by varying the reaction temperatures as well as partial pressures. More importantly, kinetic Monte Carlo simulation will enable us to examine the collective effects of various competing reaction steps which would be difficult to analyze in the quantum chemical simulation of a single reaction step.

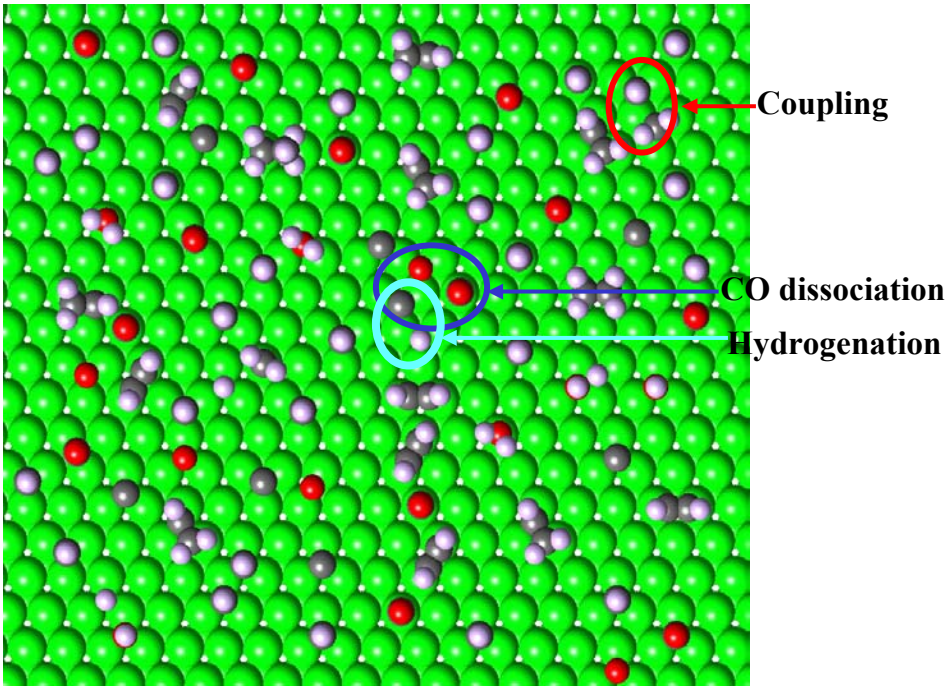

Figure 10. Schematic of possible reaction events for a kinetic Monte Carlo simulation.

VIII. REFERENCES

[1] Fischer, F.; Tropsch, H. *Brennst. Chem.*, **1923***, 4, 276*.

[2] Anderson, R. B. *The Fischer-Tropsch Synthesis*, Academic Press, New York, **1984**.

[3] Iglesia, E.; Reyes, S. C.; Madon, R. J.; Sloled, S. L. *Adv. Catal.* **1993**, 39, 221-302; Iglesia, E. Appl. Catal. **1997**, 161, 59-78.

[5] Thomas, J. M.; Thomas, W.J. *Principles and Practics of Heterogeneous Catalysis*; VCH: Weinheim, **1997**.

[6] Van der Laan, G. P.; Beenackers, A. A. C. M. *Catal. Rev. – Sci. Eng.*, **1999**, 41, 255-318.

[7] Dry, M. E. *Catal. Today*, **2002**, 71, 227-241.

[7] Horn, K.; Bradshaw, A.; Jacobi, K. *Surf. Sci*. **1978**, 72, 719.

[8] Vannice, M. A. In *Catalysis: Sciennce and Technology, Vol. 3*. Springer-Verlag, Berlin, **1982**; chapter 3.

[9] Payne, M. C.; Teter, M. P.; Allan, D. C.; Arias, T. A.; Joannopoulos, J. D. *Rev. Mod. Phys.* **1992**, *64,* 1045-1097.

[10] Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558-561.

[11] Kresse, G.; Hafner, J. *Phys. Rev. B* **1994**, *49*,14251-14269.

[12] Kresse, G. a. J. F. *Comp. Mat. Sci.* **1996**, *6*, 15-50.

[13] Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169-11186.

[14] Kresse, G.; Furthmüller, J. *Comp. Mat. Sci.* **1996**, *6*, 15.

[15] Vanderbilt, D. *Phys. Rev. B* **1990**, 41, 7892.

[16] Perdew, J. P. C., J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Frolhais, C. *Phys. Rev. B* **1992**, *46*, 6671-6687.

[17] Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188-5192.

[18] Mills, G.; Jonsson, H.; Schenter, G. K. *Surf. Sci.* **1991**, *324*, 305.

[19] Lahtinen*,* J.; Vaari, J. Kauraala, K. Soares, E. A.; Van Hove, M. A. *Surf. Sci.* **2000**, 448, 269-278

[20] Gierer, M.; Bludau, H.; Over, H.; Ertl, G. *Surf. Sci.* **1996***,* 346, 64-72.

[21] Morikawa, Y.; Mortensen, J. J.; Hammer, B.; Nørskov, J. K. *Surf. Sci*. **1997**, 386, 67-72.

[22] Geerlings, J. J. C.; Zonnevylle, M. C.; De Groot, C. P. M. *Surf. Sci.* **1991**, 241, 302-314.

[23] Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis,* Wiley, New York, **1994**.

[24] Masel, R. I. *Principles of Adsorption and Reaction on Solid Surfaces*, Wiley, New York, **1996**.

[25] Geerlings, J. J. C.; Zonnevylle, M. C.; De Groot, C. P. M. *Surf. Sci.* **1991**, 241, 315-324.

[26] Guczi, L.; Sundararajan, R.; Koppany, Zs.; Zsoldos, Z.; Schay, Z.; Mizukami, F.; Niwa, S. *J. Catal*. **1997**, 167, 482-494.

[27] Tsubaki, N.; Sun, S.; Fujimoto, K. *J. Catal*. **2001**, 199, 236-246.

[28] Ge, Q.; Desai, S.; Neurock, M.; Kourtakis, K. *J. Phys. Chem*. **2001**, 105, 9533-9536.

[29] Ciobîcă, I. M.; Frechard, F.; Van Santen, R.A.; Kleyn, A.W.; Hafner, J. *Chem. Phys. Lett.* **1999**, 311, 185-192.

[30] Ciobîcă, I. M.; Frechard, F.; Van Santen, R.A.; Kleyn, A.W.; Hafner, J. *J. Phys. Chem.* **2000**, 104, 3364-3369.

[31] Claeys, M.; Van Steen, E. *Catal. Today* **2002**, 71, 419-427.